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GROWTH AND HARDENING OF ALKALI HALIDES FOR USE IN INFRARED LASER WINDOWS

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Growth and Hardening of Alkali Halides for Use in Infrared Laser Windows

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ABSTRACT

A Reactive Atmosphere Processing Bridgman KCl crystal growth system has been placed in operation. This system uses the now conventional CCl_4 treatment method. The resultant undoped KCl crystals show a 10.6μm absorption of 0.0004 cm^{-1}. Flow stress measurements as a function of radiation damage on KBr_xI_{1-x} crystals have been started. A system for measuring the flow stress as function of temperature has been completed.

KBr(x) I(1-x)

I. INTRODUCTION

This project was initiated to study the effects of impurity doping and electron irradiation on the mechanical and optical properties of alkali halides. Our group has concentrated its efforts on KCl, which has been shown to be one of the most promising materials for use in CO_2 laser windows. A significant part of the Oklahoma State University project involves crystal growth. A second major area consists of determining changes in mechanical and optical properties of KCl doped with selected impurities, irradiated with 1.5 MeV electrons or treated in one of several other ways. 10.6μm optical absorption measurements are carried out in cooperation with AFCRL and other laboratories.

II. CRYSTAL GROWTH

A. Objectives

The crystal growth phase of this project has three main objectives: 1) To provide single crystals for mechanical and optical measurements of pure, doped and irradiated alkali halides. 2) To provide crystals grown by both the Bridgman and pulling techniques from different starting materials in order to determine the effects of these factors. 3) To provide crystals to other laboratories.

B. Reactive Atmosphere Processing

Recent work has shown that crystals grown from a KCl melt which was in contact with a halogen bearing inert gas atmosphere typically have lower 10.6μm optical absorption coefficients.[1,2] Pastor and Braunstein[1] have developed a technique in which CCl_4 vapor in an Ar carrier gas flows past the melt in a Bridgman crystal growth system. This method, called Reactive-Atmosphere-Processing (RAP) yields KCl crystals with 10.6μm absorption

coefficients in the low $10^{-4}cm^{-1}$ range. Because our crystal pullers are incompatible with the reactive atmosphere we have developed a pretreatment system.[3] This pretreatment has lowered the 10.6μm absorption coefficient for crystals pulled in our sealed inert gas systems from $4 \times 10^{-3}cm^{-1}$ to around $2 \times 10^{-3}cm^{-1}$. We believe that this lack of success is due to recontamination from the gas in the pulling furnace and have ordered a Ti gettering system to purify the gas. Consequently we have suspended the growth of RAP pretreated KCl pending the arrival of the gettering furnace.

A conventional RAP-Bridgman system has been completed and placed in operation during this quarter. The system is similar to the one described by Klein[2] and is shown schematically in Figure 1. Our current growth procedure is as follows. The vitreous carbon crucible is filled with Baker Analyzed KCl powder which has been stored at $150^{o}C$ and then placed in the Mullite tube growth chamber. The growth chamber is purged with Ar for two hours and then the CCl_4 bubbling is started for the growth run at a rate of 10-12 bubbles/minute. During the week long run this flow rate uses about $10\ cm^3$ of CCl_4. The temperature of the furnace is then raised to $300^{o}C$ and the furnace is raised at 15mm/hr to mix the gas with the melt. The cycle is repeated at $600^{o}C$. After the $600^{o}C$ cycle is completed the furnace temperature is raised to $900^{o}C$ to melt the KCl and the growth run is started at a furnace lift rate of either 1.5mm/hr or 0.75mm/hr. After completion of the 15 cm growth run, the furnace is programmed down to room temperature. The crystals, which often have a few bubbles on their surface slip freely from the crucible. A list of the RAP-Bridgman grown KCl crystals is given in Table 1.

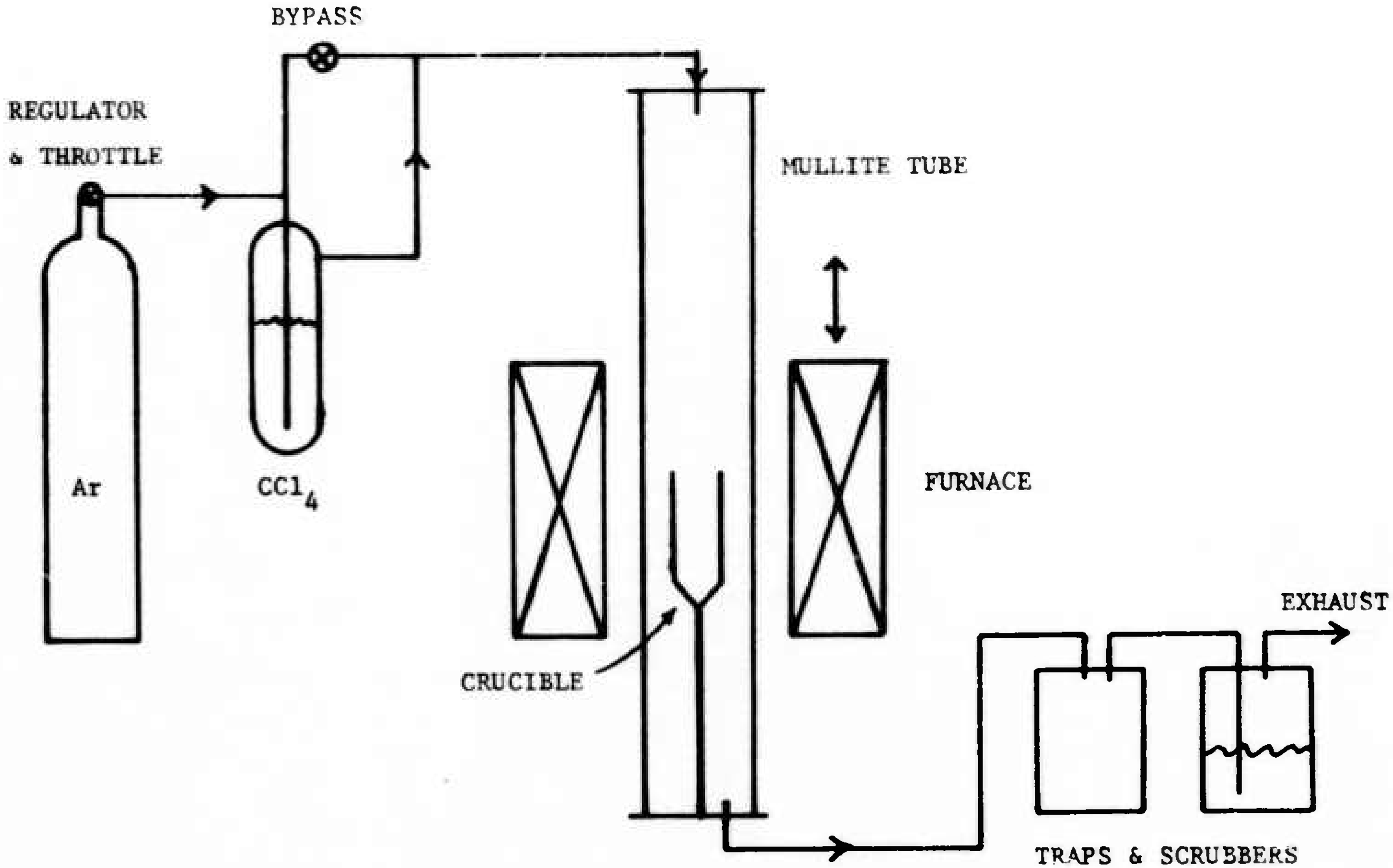

Figure 1. RAP Bridgman KCl Growth System.

Table 1. RAP-Bridgman KCl Crystals

Boule No	$\beta_{10.6}(cm^{-1})$	$C_{OH}(\mu g/g)$
052074[†]	—	≈1
062074	0.00044	<0.02
070174	0.00038	<0.02
070974	—	—
071874	—	—

[†]No CCl_4 treatment

Table 1 also gives the OH^- concentration and the absorption coefficient at 10μm. Dislocation etch pit measurements on boule 070974 indicate 1×10^5 to 2×10^5 dislocations/cm^2. The crystals were prepared for the optical measurements by removing the ends with a string saw and then water polishing them flat. They were given a final chemical polish in concentrated HCl. The OH^- concentration was estimated from the 204 nm band. These crystals also show the characteristic Pb band at 272 nm, from which an estimated Pb concentration of 0.5μg Pb/g KCl is obtained. There are additional Pb bands near 200 nm which obscure the OH band. It is interesting to note that our crystals pulled from melts of the same starting materials do not show any Pb absorption. The 10.6μm absorption coefficients were measured calorimetrically by H. Lipson and P. Ligor at AFCRL. The results show the expected reduction in absorption due to the RAP crystal growth. Work is continuing to refine the crystal growth parameters for this system. A Ti getter will be added during the next quarter to treat the Ar gas for both the crystal pullers and for the RAP Bridgman system.

C. Alloy Crystals

During this quarter we have grown several reagent grade alloy crystals.

These are a KCl:Ag crystal for thermal conductivity tests and two $KBr_{0.55}I_{0.45}$ crystals. The KBr_xI_{1-x} crystals are for radiation strengthening measurements.

III. EFFECT OF RADIATION DAMAGE ON THE 10.6μm ABSORPTION

The defects in alkali halides caused by ionizing radiation have been shown to cause significant strengthening in both single crystals[4,5,6] and polycrystalline material.[3] The defects introduced are F centers, halogen vacancies with a trapped electron, F aggregate centers and an equivalent number of halogen interstitials which have recently been shown to cluster in long <100> oriented needles in KCl.[7] Since F centers are symmetrical defects the strengthening is caused by the interstitial clusters.[4,8] Since radiation hardening is a possible strengthening mechanism for KCl CO_2 laser windows the effect of the damage on the 10.6μm must be considered. We have a cooperative program with H. Lipson at AFCRL to investigate the 10.6μm absorption of KCl as a function of radiation damage. Our earlier investigation in this area have been hampered by the high intrinsic 10.6μm absorption, 0.002 cm^{-1}, of our KCl crystals. Preliminary results on these crystals are given in Table 2.

Table 2. β(10.6) of Irradiated KCl Crystals

Crystal	$n_f(10^{16} cm^{-3})$	β cm^{-1}	Irradiation
121073A	0	0.002	None
121073B	20	0.009	1.5 MeV electrons
121073C	33	0.0096	1.5 MeV electrons
121073D	56	0.0112	1.5 MeV electrons
042774A	0	0.002	None
042774B	1.7	0.0035	γ ^{60}Co
042774C	25	0.0056	γ ^{60}Co

The electron irradiated samples, 121073, were approximately 2 cm diameter by 0.5 cm thick. They were wire sawed, water polished and chemically polished in HCl. The irradiations were carried out on the OSU Van de Graaff. The penetration depth for 1.5 MeV electrons is only 2.5 mm so the irradiation was done from both sides of the crystal. The γ irradiated samples, 042774, were approximately 2 cm diameter by 2 cm thick and were irradiated at Oak Ridge National Laboratory. It should be noted that the increase in absorption observed for sample 042774C is approximately half that observed for 121073C even though they have comparable amounts of radiation damage as determined from their F center concentrations. The calorimetric absorption measurements were performed at AFCRL. The samples were HCl polished just before the absorption measurements were made. We are planning to repeat these measurements for both electron and γ irradiation on our RAP grown KCl crystals that have a base absorption of 0.0004 cm^{-1}.

IV. MECHANICAL PROPERTIES

The mechanical properties efforts on this project are directed towards the investigation of the effects of dopants and radiation damage on the yield strength and hardness of KCl and other alkali halides window materials. To date all of our tests have been carried out at room temperature. Since, in actual use, the laser window will experience temperatures both above and below room temperature we feel that is important to extend the strength measurements to both higher and lower temperatures. During this quarter we have constructed a jig for the Instron that will allow the flow stress to be measured under compression for temperatures up to a few hundred ^{o}C above room temperature. The jig consists of two stainless steel parts threaded to the crosshead and load cell respectively, with the sample placed

between them. A cylindrical heater and guard ring which surrounds the posts will be used to heat the system to the desired temperature. The construction of the system has been completed and it will undergo calibration tests early next quarter.

The effect of radiation damage on the strength of KBr_xI_{1-x} alloy crystals should be particularly interesting. Hobbs, <u>et al</u>.[7] have found from electron microscope studies that the interstitial clusters in KCl and KBr are in the form of long <100> needles but in KI the needles have widened into rounded clusters. Recently we have reported that the flow stress of irradiated KBr_xCl_{1-x} alloy crystals goes as the square root of the F center concentration.[6] This result is consistent with the <100> needles which widen slightly as the system goes from KCl to KBr. Hobbs and Howitt have found that the flow stress of irradiated KI goes as the fourth root of the F center concentration consistent with the rounded interstitial clusters observed in KI.[9] We have prepared a $KBr_{0.55}I_{0.45}$ alloy crystal in an attempt to test the irradiation dependence of the flow stress intermediated to the needle like clusters in KBr and the rounded clusters in KI. Preliminary results on the resolved flow stress, τ_r and the Vickers microhardness, HV of this crystal are given in Table 3. The same quantities are also given for one of our RAP grown KCl crystals.

Table 3. Mechanical Properties of $KBr_{0.55}I_{0.45}$ and KCl

Crystal	$\tau_r(MN/m^2)$	$HV(kg/mm^2)^{\dagger}$
$KBr_{0.55}I_{0.45}$	18	25.3
KCl(Boule 070974)*	1.6	10.2

†15 g. load, *RAP-Bridgman grown

The resolved flow stress and Vickers hardness for KBr_xI_{1-x} sample are slightly higher than the values we found for the KBr_xCl_{1-x} system. The values for the RAP-Bridgman grown KCl crystal are comparable to those found for our untreated crystals.

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